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CYCLONE-ELECTROTHERMAL METHODS OF PROCESSING COPPER AND POLYMETALLIC MATERIALS: BEHAVIOR OF VOLATILE METALS UNDER CONDITIONS OF CYCLONE SMELTING OF POLYMETALLIC SULFIDE ORE

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CYCLONE-ELECTROTHERMAL METHODS OF PROCESSING COPPER AND POLYMETALLIC MATERIALS

[Tsiklonno-elektrotermicheskiye sposoby pererabotki mednogo i polimetallicheskogo syr'ya]

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This volume contains articles summarizing the results of investigations of processing the copper and polymetallic concentrates and other products of nonferrous metallurgy by the cyclone method. The results of theoretical studies of the technology of cyclone smelting of sulfide concentrates are also included. Certain structural features of a cyclone facility for direct-flow and separated outflow of the smelting products and of gas are described. Also, technological characteristics are given for smelting of copper concentrates of Central Kazakhstan, industrial concentration products of the lead-zinc ores, and oxidized materials.

The material in this volume will be of interest to scientists, workers in metallurgical plants who investigate methods of processing sulfide concentrates in pulverized form, and to instructors and students in the institutions of higher learning.

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BEHAVIOR OF VOLATILE METALS UNDER CONDITIONS OF CYCLONE SMELTING OF POLYMETALLIC SULFIDE ORE*

S.M. Kozhakhmetov, I.I. Penzimonzh and Z.T. Tumarbekov

Investigations of the cyclone method of smelting as applied to various polymetallic sulfide concentrates have demonstrated the possibility of obtaining considerable fractions of lead, zinc, cadmium, and rare metals from their concentrations in dusts and sublimates [1].

From the point of view of the most complete conversion of volatile metals and their compounds into the gaseous phase, the cyclone process has a number of advantages when compared with other existing methods. Out of these advantages one has to point out first of all, the possibility of obtaining in the cyclone very high temperatures, of the order of 1600-1700°. Such high temperatures ensure reaching considerable vapor pressures of many metals and their compounds.

The intensification of sublimation processes in cyclones is also connected with the presence of turbulent currents in the smelting facility which facilitate a thorough intermixing of gaseous and solid phases, and with the possibility of regulating the composition and output of the smelting products. These factors create

*Based on material of the lecture delivered at the All-Union Scientific-Technical Conference on Cyclone and Power Engineering Processes, held in Moscow in November, 1966 (MEI).

the most favorable conditions for intensification of the processes of heat transfer and mass transfer in the smelting area, and thereby lead to maximum conversion of the volatile components of the charge into the gaseous phase.

In order to find the conditions of maximum sublimation of volatile metals in the cyclone smelting of polymetallic ores, it is necessary to have data on the kinetics of volatilization, and the effect of temperature and composition of the gaseous phase on the sublimation process of the metal compounds.

In this connection, the Institute of Metallurgy and Enrichment of the AN Kazakh SSR has been conducting for a number of years studies of the kinetics of volatilization of sulfides of lead, zinc, cadmium and some rare metals, in the 1000-1500° temperature range, and in an atmosphere of various gases.

The present paper presents brief results of these studies and some considerations on the process of sublimation under conditions of the cyclone process.

Experimental Procedure

To determine the rate of volatilization of sulfides in the atmosphere of various gases and at high temperatures, we selected and tested a laboratory facility, which was based on the principle of the continuous weighing of investigated sulfide during the experiment. The scheme of the facility, its description and the experimental procedure have been given in published works [2, 3].

Natural minerals — galenite and sphalerite — carefully chosen and cleared from inclusions of other minerals were utilized as initial materials. During the study of the rate of volatilization of the sulfides of cadmium, indium and rhenium, we utilized artificially prepared samples.

Rate of Volatilization of Lead Sulfide

The majority of results on volatilization of lead sulfide, contained in the literature, were obtained at a temperature of 1000-1100°. There have been no investigations of the sublimation of lead sulfide at higher temperatures.

The present investigations of the rate of volatilization of lead sulfide were carried out in the 900-1400° temperature range in the atmospheres of argon, carbon monoxide, carbon dioxide, and sulfur dioxide.

To find the weight change of lead sulfide and to determine the temperature of the beginning of its volatilization, the first series of experiments was conducted at a continuously increasing furnace temperature from 20 to 1200°. It was established in this series that the sublimation of lead sulfide in the atmospheres of all these gases takes place in the 800-840° range.

The temperature dependence of the rate of volatilization of lead sulfide, and the effect of composition of the gaseous phase, were studied at the temperatures 900, 1000, 1100, 1200, 1300 and 1400°. The experimental results obtained are presented in Figure 1.

For the region of high temperatures (after the melting of sulfide), in the 1170-1400° range, we found from experimental data equations of the temperature dependence of the rate of volatilization. They, in turn, served to calculate the corresponding values of the apparent activation energy of the process of sublimation of lead sulfide:

$$\lg v_{Ar} = -\frac{9580}{T} + 8{,}22;\ E_{Ar} = 44500 \text{ cal/mole}$$

$$\lg v_{CO} = -\frac{6920}{T} + 6{,}52;\ E_{CO} = 31700 \text{ cal/mole}$$

$$\lg v_{CO_2} = -\frac{7170}{T} + 6{,}90;\ E_{CO_2} = 32600 \text{ cal/mole}$$

$$\lg v_{SO_2} = -\frac{6700}{T} + 6{,}55;\ E_{SO_2} = 30700 \text{ cal/mole}$$

To determine the effect of carbon monoxide, carbon dioxide and sulfur dioxide in the gaseous phase on the rate of volatilization of lead sulfide, we conducted a series of experiments at a temperature of 1100°. The contents of these gases in their admixture with argon varied within 0-100%. The results of this series of experiments have shown that, with an increase of the content of carbon monoxide, carbon dioxide and sulfur dioxide in the mixture, there is an increase in the rate of volatilization, the maximum value of which is reached in the atmosphere of pure gases.

Both the character of curves of the temperature dependence of the rate of volatilization, and the values of the apparent activation energy of the sublimation of lead sulfide, have a similar mechanism of volatilization of sulfide in the atmosphere of all gases. The volatilization of lead sulfide occurs, apparently, as a result of its sublimation.

Comparison of the volatilization rate of lead sulfide (Figure 1), obtained as a function of temperature and composition of the gaseous phase, reveals that the influence of these factors on the volatilization process varies. Thus, a change in the composition of the gaseous phase affects very little the rate of volatilization of lead sulfide. The basic factor which determines the velocity and degree of its volatilization is the temperature.

Rate of Volatilization of Zinc Sulfide

The least volatile component of polymetallic copper concentrates is zinc, which is present essentially in the form of sulfide. Although many studies have been devoted to the behavior of zinc, the existing data on the volatilization of zinc from sulfide are rather contradictory and refer to temperatures up to only 1200°. It is only in the last years that investigations were initiated on the process of volatilization of zinc sulfide at high temperatures [4-6].

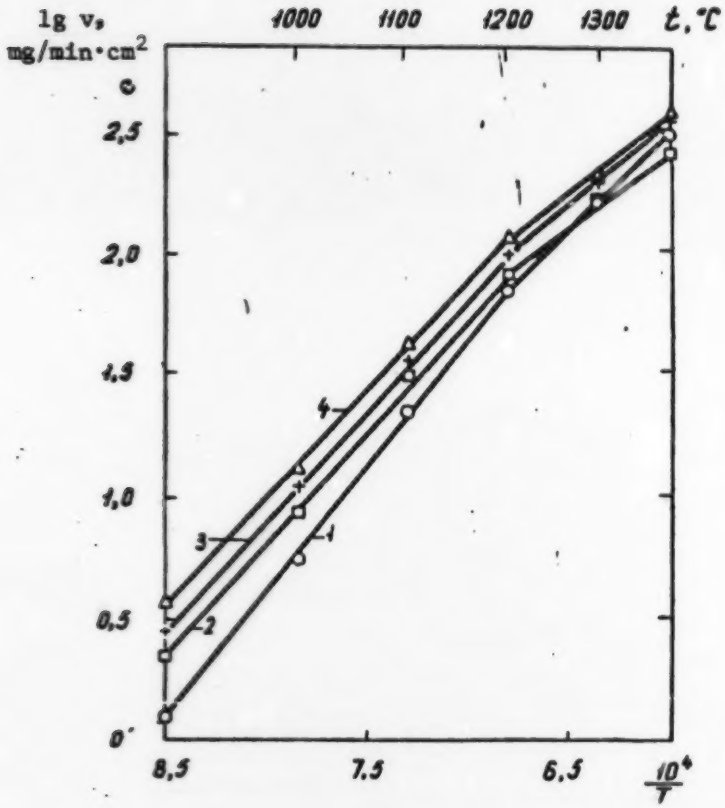

Figure 1. Effect of temperature and composition of the gaseous phase on the rate of volatilization of lead sulfide. 1 - argon; 2 - carbon monoxide; 3 - sulfur dioxide; 4 - carbon dioxide.

Our investigations of the volatilization process of zinc sulfide, as a function of temperature and composition of the gaseous phase, were conducted in the atmosphere of argon, carbon monoxide, hydrogen, carbon dioxide, and sulfur dioxide. The temperature range was 1100-1500°.

The results of experiments carried out at continuously increasing temperature have revealed that zinc sulfide begins to show noticeable volatilization at 870-900° in the atmosphere of hydrogen, at 1090-1100° in the atmosphere of carbon monoxide, at 1080-1100° in the atmosphere of carbon dioxide and sulfur dioxide, and at 1260-1280° in the atmosphere of argon.

The effect of temperature and composition of the gaseous medium on the rate of volatilization of zinc sulfide is presented in Figure 2.

On the basis of the experimental results obtained at 1100-1500°, the following equations were derived for the temperature dependence of the rate of volatilization of zinc sulfide, and the following apparent activation energies were computed for its volatilization in the atmospheres of these gases:

$$\lg v_{Ar} = -\frac{13366}{T} + 7{,}15;\ E_{Ar} = 61000 \text{ cal/mole}$$

$$\lg v_{CO_2} = -\frac{8550}{T} + 4{,}50;\ E_{CO_2} = 39000 \text{ cal/mole}$$

$$\lg v_{SO_2} = -\frac{8600}{T} + 5{,}50;\ E_{SO_2} = 39200 \text{ cal/mole}$$

$$\lg v_{CO} = -\frac{7080}{T} + 3{,}74;\ E_{CO} = 32100 \text{ cal/mole}$$

$$\lg v_{H_2} = -\frac{8330}{T} + 5{,}40;\ E_{H_2} = 38000 \text{ cal/mole}$$

Comparison of these data shows that, in contrast to the case of lead sulfide, the rate of volatilization of zinc sulfide in the temperature range of 1100-1300° depends to a considerably greater degree on the gaseous phase composition. However, at a temperature of 1500° the values of the volatilization rate of zinc sulfide in the neutral atmosphere and in the atmospheres of carbon dioxide, sulfur dioxide and carbon monoxide converge (Figure 2). Probably, the conversion of zinc from sulfide into the gaseous phase at high temperatures is essentially due to sublimation, and thermal dissociation of zinc sulfide, according to the equations:

$$ZnS_{solid} \rightarrow ZnS_{gas}; \quad (1)$$

$$ZnS_{solid} \rightarrow Zn_{gas} + \frac{1}{2} S_2. \quad (2)$$

Since these processes are endothermic, and they do not involve gaseous reagents, their velocity will depend in principle on the temperature. The dominating role of temperature was also shown by L.M. Bochkarev and O.P. Shumilova [5] in investigations of the volatilization of zinc from sulfide in an oxidizing atmosphere in the temperature range 1300-1700°.

In contrast to the case of lead sulfide, the calculated values of the apparent activation energy of the volatilization process of zinc sulfide in a neutral atmosphere and in atmospheres of other gases show considerable differences. These differences, apparently, point to a change of the mechanism for the conversion of zinc sulfide into the gaseous phase, depending on the composition of the latter. The most intense volatilization of zinc sulfide occurs in an atmosphere of reducing gases. The relatively high rates of volatilization of zinc sulfide in atmospheres of carbon monoxide and hydrogen, as compared with the rates in other gases, are explained, apparently, by the fact that along with volatilization of the sulfide we also have its reduction, according to the equations

$$ZnS + CO \rightleftarrows Zn + COS; \quad (3)$$

$$ZnS + H_2 \rightleftarrows Zn + H_2S \quad (4)$$

with the formation of metallic zinc, the vapor pressure of which reaches one atmosphere at 907°.

As is seen from Figure 2, the volatilization of zinc sulfide is particularly intense in the atmosphere of hydrogen. Thus, a comparison of the rates of volatilization in atmospheres of carbon monoxide and hydrogen shows that the conversion of zinc sulfide into the gaseous phase in hydrogen is, as a rule, 8-9 times higher than in the atmosphere of carbon monoxide, at all temperatures. This fact, in our opinion, has the following explanation.

First, as is known, hydrogen is a considerably more active reducing agent than is carbon monoxide. Second, in the mutual diffusion of gases (in our case, the diffusing gas is the molecules of vaporizing zinc sulfide) the coefficient of diffusion in hydrogen is 4-5 times larger than in the atmosphere of carbon monoxide.

We investigated the effect of the content in the gaseous phase of carbon monoxide, carbon dioxide and sulfur dioxide on the rate of volatilization of zinc sulfide at a temperature of 1200°. The content of these gases in their mixture with argon varied from 0-100%. It was found that, whereas the rate of volatilization increases with

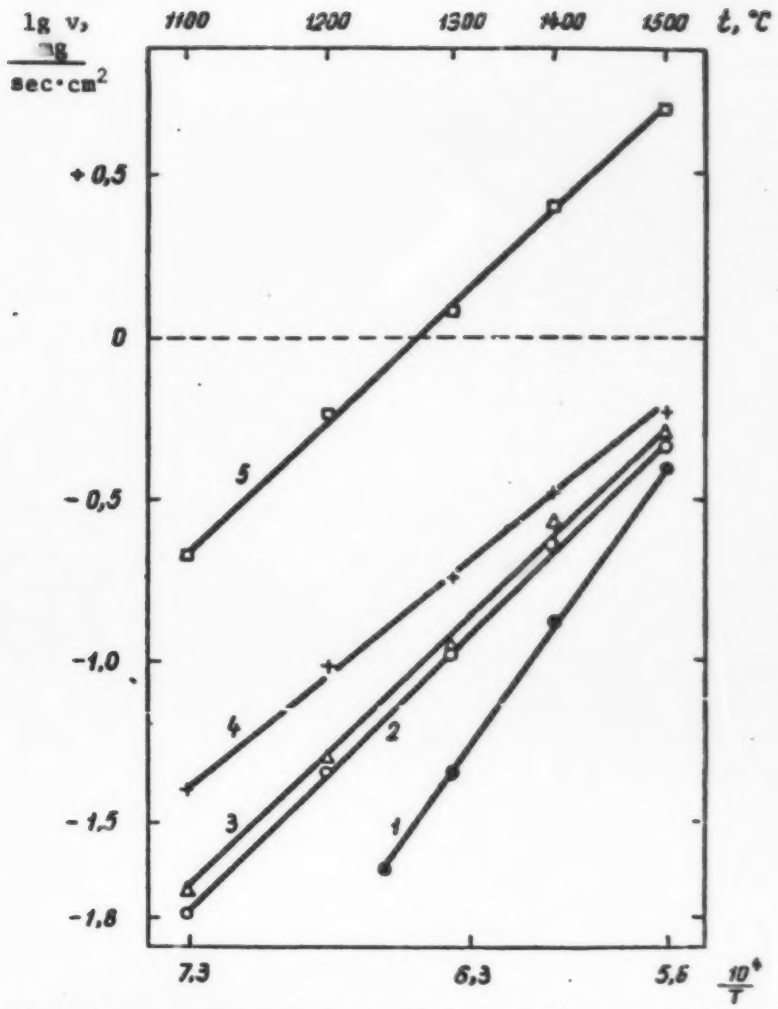

Figure 2. Effect of temperature and composition of the gaseous medium on the rate of volatilization of zinc sulfide. 1 - argon; 2 - sulfur dioxide; 3 - carbon doixide; 4 - carbon monoxide; 5 - hydrogen.

an increase of the carbon monoxide content in the gaseous phase, reaching a maximum value in the atmosphere of pure carbon monoxide, an increase of the content of carbon dioxide and sulfur dioxide enhances the volatilization of zinc sulfide only up to 50% (Figure 3). A further increase of the content of these gases in their mixture with argon leads to a certain lowering of the rate of volatilization. This behavior is due, apparently, to the oxidation of the surface of zinc sulfide.

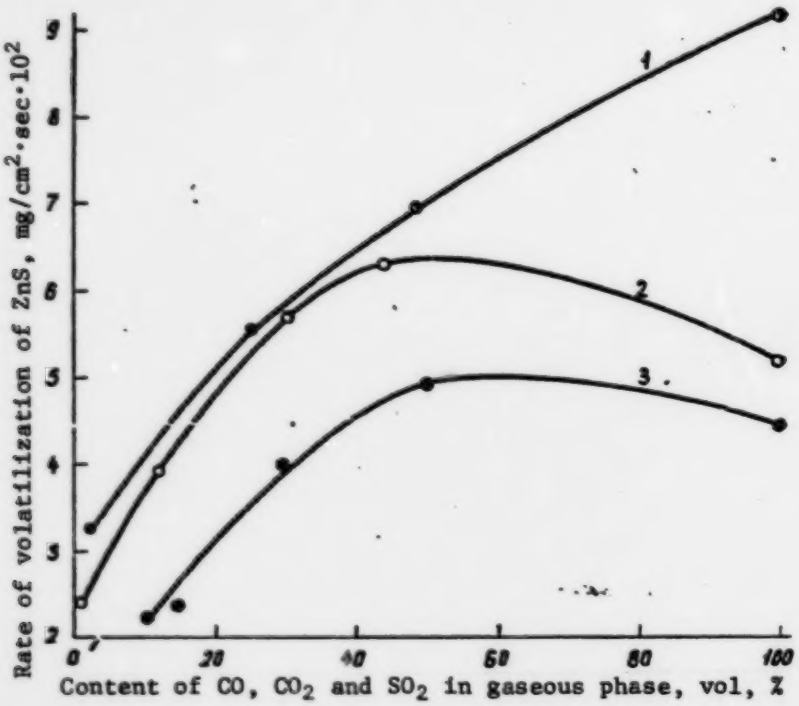

Figure 3. Effect of the content in the gaseous phase of CO (1), CO_2 (2), and SO_2 (3) on the rate of volatilization of zinc sulfide at 1200°.

As far as the role of oxygen in the volatilization of zinc from sulfide ore is concerned, this problem until now has not been sufficiently clarified. Many investigators consider [5, 7] that in the presence of oxygen in the gaseous phase the passage of zinc into the sublimate takes place basically through the interaction of sulfide with oxide

$$ZnS + 2ZnO \rightleftarrows 3Zn + SO_2. \qquad (5)$$

This conclusion is based on the experimental data from studies of the rate of interaction of zinc oxide with sulfide, when the initial materials are taken in quantities corresponding to their stoichiometric coefficients according to reaction (5), and when their mixture is heated in a crucible.

In our opinion, the probability of interaction of zinc sulfide with its oxide is insignificant under smelting conditions of copper

concentrates, containing usually not more than 7-8% of zinc. On the contrary, the formation of vapors of metallic zinc is more probable as a result of interaction of zinc sulfide with copper and copper oxide, and also the reduction of zinc oxide with sulfides of copper and iron, whose concentrations in the charge are considerably higher than the concentration of zinc sulfide.

Volatilization Rate of Cadmium Sulfide

Experiments with cadmium sulfide were carried out under the same conditions as those applied to the determination of the volatilization rate of zinc sulfide, with the exception of the temperature range, which was 1000-1400° for cadmium sulfide. It has to be noted that the behavior of cadmium sulfide, both in the atmosphere of pure gases and in the atmosphere of their mixtures with argon, was analogous to the behavior of zinc sulfide. Hence, the above discussion of the results corresponding to the rate of volatilization of zinc sulfide is also, in principle, applicable to the case of cadmium sulfide.

In contrast to zinc sulfide, the sulfide of cadmium noticeably volatilizes at 980-990° in a neutral medium, at 900-920° in a current of carbon dioxide, at 940-950° in a medium of sulfur dioxide, at 820-840° in an atmosphere of carbon monoxide, and at 610-620° in an atmosphere of hydrogen.

The influence of temperature and composition of the gaseous phase on the rate of volatilization of cadmium sulfide is shown in Figure 4. Based on these data, the equations of the temperature dependence of the rates, and the values of the apparent activation energy of the volatilization process of cadmium sulfide, are:

$$\lg v_{Ar} = -\frac{13000}{T} + 8{,}13;\ E_{Ar} = 59400 \text{ cal/mole}$$

$$\lg v_{CO_2} = -\frac{10650}{T} + 6{,}85;\ E_{CO_2} = 48700 \text{ cal/mole}$$

$$\lg v_{SO_2} = -\frac{9730}{T} + 6{,}19;\ E_{SO_2} = 44500 \text{ cal/mole}$$

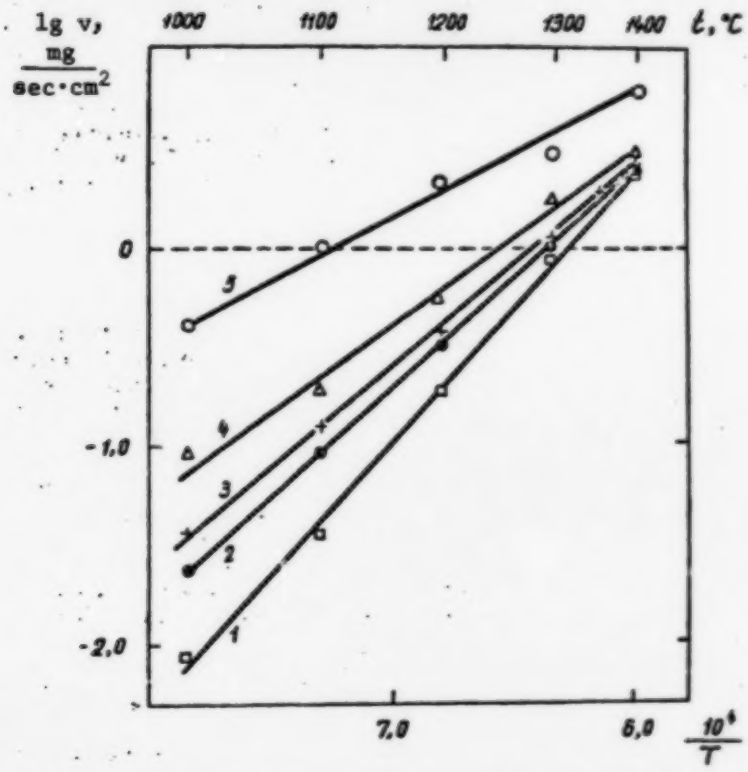

Figure 4. Effect of the temperature and composition of the gaseous phase on the rate of volatilization of cadmium sulfide. 1 - argon; 2 - sulfur doixide; 3 - carbon dioxide; 4 - carbon monoxide; 5 - hydrogen.

$$\lg v_{CO} = -\frac{10050}{T} + 6{,}53;\ E_{CO} = 46000 \text{ cal/mole}$$

$$\lg v_{H_2} = -\frac{6380}{T} + 4{,}60;\ E_{H_2} = 29200 \text{ cal/mole}$$

Behavior of the Sulfides of Indium and Rhenium During their Heating in a Neutral Atmosphere

The behavior of indium and rhenium under conditions of high-temperature processes of smelting of polymetallic ores has been little studied. The data found in the literature [8-10] were obtained during an investigation of the thermodynamic properties of sulfides and their volatility in a vacuum, and also during studies of the behavior of indium sulfide and rhenium sulfide in an oxidizing medium when heated to 1000°.

To obtain data on the behavior of these metals at high temperatures, we initiated studies of the kinetics of the volatilization of indium and rhenium from their sulfides. The results of the first series of experiments, carried out in a neutral medium, are briefly as follows.

Indium sulfide (In_2S_3) in an argon atmosphere begins to volatilize noticeably at temperatures of 820-850°, and the rate of its volatilization in the interval 900-1400° is 2.17 - 297.0 mg/cm^2·min. The temperature dependence of the rate of volatilization of indium sulfide is described satisfactorily by the equation:

$$\lg v = -\frac{12200}{T} + 10{,}24 \quad (900-1400^\circ).$$

During the heating of rhenium sulfide (ReS_2) in a neutral atmosphere, the weight loss continues only up to 1300°, and further increase of the temperature up to 1500° does not lead to changes in sample weight. A similar behavior of the disulfide of rhenium has been explained as due to the fact that rhenium sulfide fully dissociates into rhenium and sulfur at high temperatures [8]. This interpretation is confirmed by the chemical composition of residues after the experiments, since the content of rhenium in them reached 94.60%.

Under conditions of our experiments, we eliminated sulfur from rhenium disulfide, but we had no volatilization of rhenium.

At present we are carrying out investigations of the effect of the gaseous phase composition on the volatilization of indium and rhenium from their sulfides.

Conclusions

1. Investigations were carried out by a thermogravimetric method on the influence of temperature and composition of the gaseous phase on the rate of volatilization of the sulfides of lead, zinc, cadmium, indium and rhenium in the temperature range 1000-1500°.

2. It was established experimentally that there is a linear dependence of the rate of volatilization of sulfides on the temperature, in the coordinates $\lg v = -\frac{1}{T}$, satisfactorily described by a simplified Arrhenius equation of the type $\lg v = \frac{A}{T} + B$.

3. It was shown, that the basic factor, upon which depends the intensity of the process of sublimation of sulfides (with the exception of rhenium sulfide), is the temperature.

4. For a more detailed investigation of the behavior of volatile metals and their compounds under conditions of cyclone smelting of polymetallic ores, it is necessary to conduct both additional studies of the mechanism of sublimation processes of volatile metals, and also investigations of the smelting of various materials, simulating the aerodynamics of the process.

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